Catalytic Hydrogenation of Hydrocarbons for Gasoline Production

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ABSTRACT: *The persistent growth in the global population has accounted for the continuous increase in the use of gasoline-based automobile engines. Although the application of gasoline additives such as tetraethyl lead (TEL), oxygenates and metal carbonyls like methyl cyclopentadienyl manganese tricarbonyl (MCT) has been considered suitable for gasoline quality upgrading, the numerous challenges that include environmental pollution and destruction to catalytic converters attributed to search for better valorisation options. The hydrogenation of hydrocarbon fractions from petroleum refining is a forefront issue recently adopted by refineries worldwide. The process involves the incorporation of suitable catalytic systems under hydrogen atmosphere to upgrade hydrocarbons into similar derivatives of better gasoline properties. The paper carefully tailored a series of recently published literature on the various aspect of the hydrogen process with emphasis to catalyst design and testing, mechanisms, industrial perspective and challenges. Areas for further investigations were also discussed.*

Keywords: Hydrogenation, gasoline, catalysis, hydrocarbons, catalytic hydrogenation

1. INTRODUCTION

Hydrocarbon fuels are usually obtained from petroleum fractions. Depending on application and environmental constrain associated with production, they are blended with other specific hydrocarbon components to produce a variety of very high grade fuels.[1,2] Meanwhile, it is a well-known fact that the major components of fuel used in internal combustion engines comprise mainly of straight chain and isomers of light and medium alkanes with specific concentration

of aromatics due to environmental policies, but are good for the optimisation of octane number.[1–5] Refinery operations generally produce several streams of products that are typically quantified as functions of hydrocarbons sources used in various processes in generating high grade fuels. However, all these products contain valuable petrochemical components which at stages of productions require improved processing to extract them in more valuable forms. Research indicated that petroleum-based fuels are popularly used as a major commodity for transportation system and industrial based applications.[6,7] Research has also revealed that the global refinery construction will still grow for many decades to come despite the low margin reported for growth over supply.[8] The growth was projected historically at a high rate and that by 2025 every region of the world is expected to see a refinery conversion capacity for more valuable products growing faster than distillation with only 1.3% to 2.4% per annum for distillation compared to 2.4%–0.5% per annum for conversion as illustrated in Figure 1.
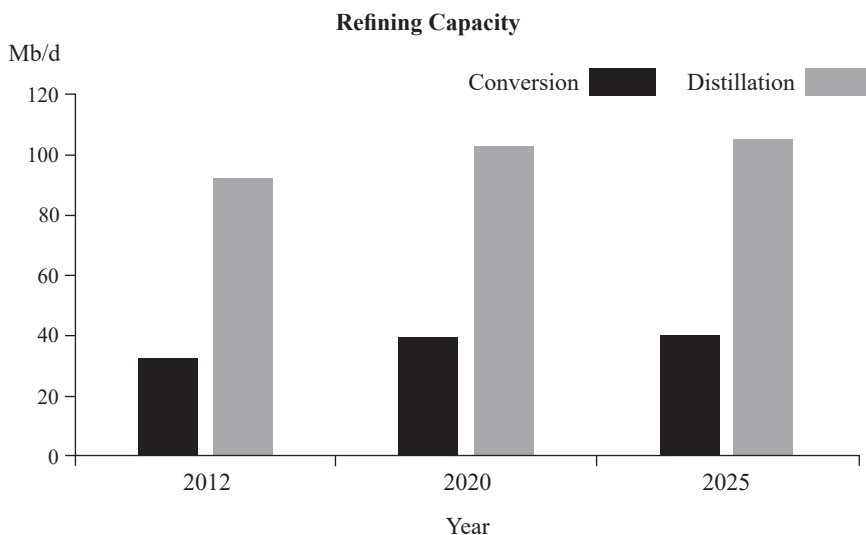

Figure 1: Global refining capacity and capacity additions.[8]

Generally, the global conversion/distillation ratio had been projected to grow by ~10% annually. However, maximising the products will strongly depend on refining industries to devise a more satisfying route for production of high quality fuels especially for cetane/octane numbers and adherent to environmental constrains. For instance, the growth in the content of aromatic ring compounds in Fluid Catalytic Cracking Unit (FCCU) feedstock necessitates their conversions into more useful compounds. The naphthenic ring opening catalytic process accounts for monocyclic, dicyclic and polycyclo-paraffins which could be further converted into iso-paraffins by side chain reaction to maximise and produce quality fuel.[9]

Hydrogenation process is a well-known method to have been used in refinery over many decades. It has the advantage of converting various hydrocarbons to most valuable ones, ranging from dealkylation of aromatics, opening of naphthenic rings, hydrocracking of paraffin chains, removal of hetro-atoms and saturation of carbon-carbon bonds (see Scheme 1).[10] For instance, hydrogenation reaction can proceed through the addition of adsorbed hydrogen molecule on catalyst surface to the unsaturated bonded atom to form a corresponding saturated alkane.[11–14] It also has the advantage to open up an unsaturated ring and removal of hetro-atoms into any hydrocarbon formed molecules.[15–19]
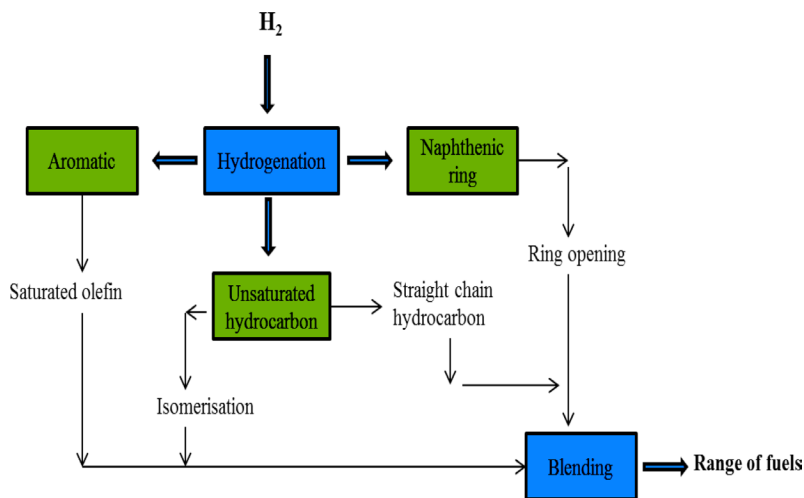
Scheme 1: Typical hydrogenation units and products for fuel range blending.

Hydrogenation is an important process in petroleum refining with an estimated economic benefit of around 6 million US dollar/year on an average scale refinery.[20] The process could also be effectively utilised in the process of coal, tar sand and shale exploration that provide cleaner burning fuels. Literature works suggested many available commercial catalysts, but the catalyst systems are typically by aimed process of the hydrogenation involved in the refinery. However, each process has individual preferential selectivity, but is mainly of Mo, Ni and Co supported alumina-based catalyst system for severe hydrogenation process is well known.[21–28] For instance, cobalt molybdenum is used for hydrodesulfurisation (HDS) and nickel molybdenum for hydrodenitrogenation (HDN) efficiency, but the efficacy of different catalysts used appears to be based on reactivity and effectiveness of the process. Meanwhile, other active materials such as catalyst systems of noble metals, zeolites, mesoporous molecular sieves and some other non-oxide supports have also been evaluated.[29–35]

The issues of hetro-atom removal with respect to the hydrogenation of the olefins require a special control mechanism for optimum octane rating.[19] However, selectivity of the process is influenced by many factors such as the catalyst promoters for HDS, but the effect is also reported for the olefins hydrogenation and the aromatic counterparts.[36–41] The structure of the individual reactants has also been pointed out for the effective reactivity of the catalyst.

The paper presents a review on the role of heterogeneous catalyst systems for the hydrogenation (i.e., upgrading) of hydrocarbon-based fuels into blending grade ones. Emphasis would be given to catalyst development and activity evaluation during hydrogenations of unsaturated hydrocarbons, aromatics and naphthenic rings opening into paraffins. The paper will provide a baseline for identifying the progress made and the ways forward. The use of catalysts is widely known for the processes. However, the main catalyst systems were identified as cost effective especially for the necessity for conversion of hydrocarbons to more useful compounds and environmental sustainability that would be achieved. Therefore, the paper will mainly focus on these catalytic systems. Noble metals (i.e., platinum group metals like Pt, Pd, Ru, etc.) and composite transition metal catalysts based on nickel, molybdenum, and cobalt and their various supported analogues were reportedly studied for hydrogenation of unsaturated hydrocarbons, aromatics and the naphthenic ring opening. The paper covers concise details on these materials, with emphasis on their activities and operation conditions. Hydrocarbons conversion into iso-paraffins on the catalyst acidic sites and factors responsible for catalyst deactivation would also be discussed.

2.   HYDROGENATION REACTION IN PETROLEUM INDUSTRY

The hydrogenation reactions of hydrocarbon feedstocks are extensively carried out in petroleum refineries. The practice usually employs the use of metallic/acidic catalysts at elevated temperature and hydrogen pressure conditions. The hydrogenation process in refinery constitutes versatile activities of a number of important reactions, which includes the removal of hetro-atoms such as sulphur, nitrogen and metals, saturation of olefins and aromatic, opening of naphthenic rings, and to improve the H/C ratio in hydrocarbon range fuels. The main primary objectives are as follows:

1. Removal of sulphur from gasoline blending components to meet the recent clean fuel specifications and downstream processes.

2. Removal of sulphur from diesels and kerosene for heavy engines and home heating, respectively.

3.   Conversion of kerosene to jet fuel through mild aromatic saturation.

4.   Removal of hetro-atoms for efficient catalyst activity in FCC.

5.   Hydrocarbon rings opening and saturation of olefins into paraffin which could further be converted into iso-paraffins for cetane/octane improvement.
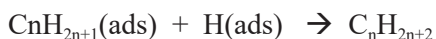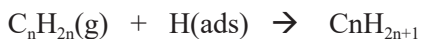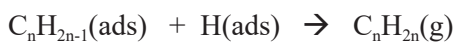
In a generic form, these refinery hydrogenation processes could be presented as shown in Scheme 2 given below:
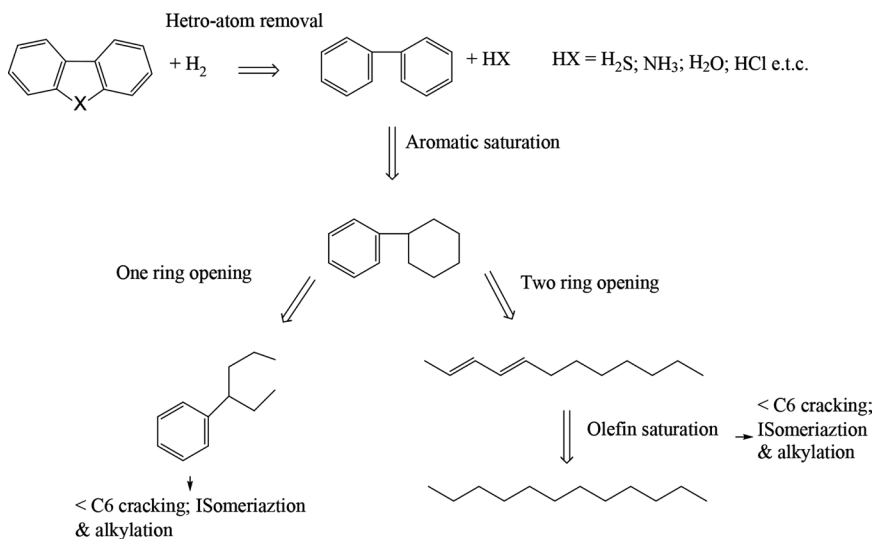
Scheme 2: A generic form of hydrogenation reactions in refinery.

2.1   Hydrogenation of Unsaturated C4-C8 to Alkanes

The hydrogenation reaction involved the addition of absorbed hydrogen on the catalyst surface to the unsaturated hydrocarbon in the feed and producing the corresponding paraffin. A simple generic mechanism is outlined in Scheme 3 below.

$$C_nH_{2n-2}(g) \ + \ H(ads) \ \rightarrow \ C_nH_{2n-1}(ads)$$

$$C_nH_{2n-1}(ads) \ + \ H(ads) \ \rightarrow \ C_nH_{2n}(g)$$

$$C_nH_{2n}(g) \ + \ H(ads) \ \rightarrow \ CnH_{2n+1}$$

$$CnH_{2n+1}(ads) \ + \ H(ads) \ \rightarrow \ C_nH_{2n+2}$$

Scheme 3: Illustrative mechanism for hydrogenation of hydrocrabons.

Hydrogenation of hydrocarbon is exothermic and produces a significant amount heat.[42] However, alkynes are thermodynamically less stable than the respective alkene due to the nature of their bonding and strongly adsorb catalyst surfaces. Highly unsaturated hydrocarbons are sometimes hydrogenated into corresponding olefin depending on demands. Producing the desired alkene rather than the alkane, however, in catalytic hydrogenation, may be difficult because there are significant numbers of hydrogenation catalysts effective in promoting the addition of hydrogen but fewer are selective in that aspect. Palladium (Pd) is known to be a good metal candidate for selective hydrogenation of highly unsaturated hydrocarbon but even with Pd, catalysts may be partially deactivated as in Lindlar's catalyst or poisoned as in the addition of carbon monoxide in ethyne hydrogenation, to limit the production of the alkane. Although alkene hydrogenation is inhibited by the presence of alkynes, in the absence of the alkyne, research indicates that the alkene will react more rapidly.[43] Research has also shown that in a competitive environment, the alkyne can influence the reactivity of other alkynes and alkenes.[44,45] Hydrogenation of unsaturated bonds is considered a very important catalytic technique in refinery operations. Ideally, hydrogenation can be performed at low temperature of ~100°C or below and relatively low hydrogen pressure of typically 10–15 bar in a catalyst system constituting noble metal such as Pt, Pd, Rh and Ru. However, catalyst system constituting metals such as Ni, Co, Sn and Mo, etc., required a high temperature and high hydrogen pressure but are cheaper and more accessible.

One of the early hydrogenation reactions was performed by Bond.[11] In the study, the reaction of ethylene and propylene was demonstrated. The reaction was performed using Pt/Al_2O_3-support and Ir/Al_2O_3-support in mild temperatures ~20°C–150°C to observe the interaction of the olefin and the deuterium and compare to hydrogen feed to understand efficacy of the used catalyst on the hydrogenation activity of the tested olefin reactants. The interaction of the tested catalyst gives only small amount of deuteron-olefin and HD [ratio p(deuteron-olefin)/p(paraffin)] <0.1 the rate of double-bond migration relative to hydrogenation are low but the relative of olefin exchange generally increases with decreasing $P_{H2,D2}/P_O$ and increasing temperature.

Boitiaux et al. worked on the liquid phase hydrogenation of unsaturated hydrocarbon 1-butene, 1,3-butadiene and 1-butyne at 20°C and 20 bar.[14] Roughly 80% conversion was obtained during the hydrogenation of 1-butene to butane over the Rh/Al_2O_3 catalyst. However, unlike reactions over Pt/Al_2O_3, butane was not the sole product formed because double bond shift and isomerisation are also observed with Rh/Al_2O_3.[46] High conversion was also observed with 1,3-butadiene over the Rh catalyst, and several other products were also observed in addition to the main

1-butene product which includes tran-2-butene, butane and cis-2-butene. 1-butene hydrogenation also begins after a high conversion of 1,3-butadiene is achieved. The hydrogenation of 1-butyne over Rh catalyst generates only 1-butene which appears at the very beginning of the reaction. The hydrogenation reactions with Rh-catalyst are very sensitive to metallic dispersion compared with Pt and Pd catalyst. However, hydrogenation of the 1-butyne over the complete range dispersion Rh-catalyst close to 100% deactivates the catalyst. The hydrogenation of 1-butene is completely in line with the other tested catalyst with increasing activity order Pt < Pd < Rh. This order remains the same with Pt and Rh (Pt < Rh) for butadiene and butyne hydrogenation but Pd is by far more active than others.

2.2   The Hydrogenation Activity

### 2.2.1   Hydrogenation in ring opening for gasoline fuel

Ring opening reactions are primarily performed in the refinery to meet an increased demand in diesel products. For example, refineries in Europe have the option to blend light cycle oil (LCO) fractions from Face Centred Cubic (FCC) process to maximise the diesel production, but this does not generally meet the requirements currently placed on diesel specifications. This is because due to high amount of polyaromatics compound around ~48%–69% and a low cetane number of ~18–25 which contradicts the European guidelines that limit the polyaromatic blending speciation to ~11% and a minimum cetane number of 51.[47] Therefore, the polycyclic components are hydrotreated and more significantly lowered by hydrogenation to improve the cetane number. However, ring opening was employed thereafter to further improve the cetane number and enable the light cycle oil to be more significantly used in the diesel blending. This is illustrated in Scheme 4.
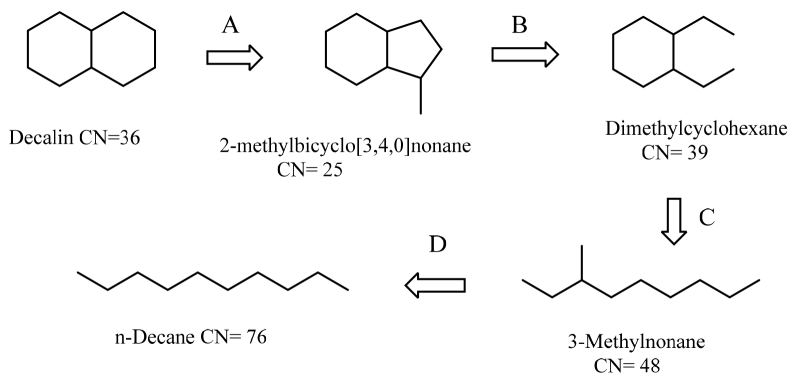
Scheme 4: Improving the cetane number of fuel via ring opening process.

Ring opening significantly increases the cetane number of a molecule as illustrated, starting from aromatic cycle into ring molecule and converted to liner or mono branched paraffin all at the backbone of hydrogenations. Ring opening is selective towards the desire paraffin and could be done using metal, acid and bifunctional catalyst raging from simplest methylcyclohexane to a complex naphthenic ring molecule. The reaction of complex napthenic ring such as decalin and tetralin is often hindered by a number of problems in the reaction pathways due to complexity and nature of the rings. Therefore, the reaction requires more details to understand the ring opening mechanism and suitable catalyst system.[48]

It had been reported that some of the ring opening processes occur via sequential dehydrogenation, protonation and protolytic-dehydrogenation which then crack to produce the open structured hydrocarbons. Others include isomerisation reaction, hydrogenation and hydride transfer because the reaction mechanism involves hydrogenation acid mediated cracking and isomerisation. However, the widely known method is performed via acid catalysed ring opening widely studied on zeolites. Several studies have been performed to study the acid catalysed ring opening of decalin which revealed that decalin opening using zeolites occurs by ring contradiction via isomerisation as illustrated in Scheme 5.[49–53]
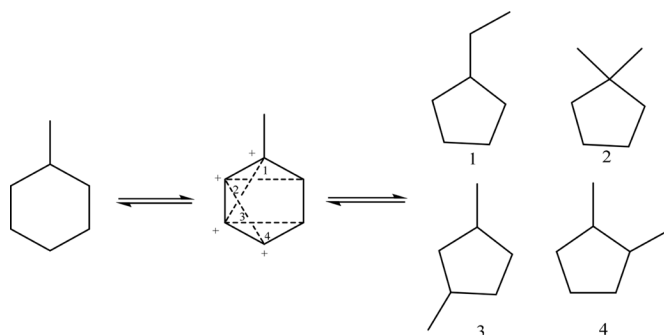
Scheme 5: Illustration of ring contradiction and skeletal isomerisation using cyclohexane as a model compound.

Studies by Kubička et al. reveals that the activities are usually Bronsted influential and were best obtained with moderate Bronsted acidity catalyst such as Hβ-25, Hβ-75 and HY-12 zeolite.[50] There is nearly no activity reported for catalyst with low Bronsted acidity such as MCM-41[50]. However, fast deactivation is recorded with strong Bronsted acid catalyst such as (H-mordenite-20) due to coke deposition. Generally, ring opening observed over acid catalyst proceed via the Bronsted acid sites and performed by protolytic dehydrogenation followed by carbenium ion formation through ring contradiction, β-scission, alkylation and hydride transfer.[50,54]

Selectivity of ring opening of naphthenic molecule is investigated using several metals. McVicker et al. studied the selectivity using Ru, Rh, Ni, Ir and Pt, and reported that Rh, Ni and Ru showed similar preferences over the cleaving of unsubstituted C-C bonds.[55] Ir showed high selectivity compared to the all tested metals, while Pt metal showed less selectivity but can cleave the substituted C-C bond. Approximate statistical production distributions were formulated by Gault.[56]

Another similar investigation showed that metals such as Rh, Ir, Pd and Pt may improve single hydrogenolysis among eleven studied catalysts.[57] In a cited example, hydrogenolysis of 3-methylpentane and methylcyclohexane was obtained using these metals. It was revealed that the isomerisation, C5 ring opening and closure activity of these catalysts (Rh, Ir, Pd and Pt) could be correlated to their FCC structure and atomic dimensions. However, when Co, Ni, Ru, Cu, Re, Ag and Os were employed, multiple fragmentations were observed leading to formation of less than 7-carbon atoms. Meanwhile, literature showed that Ir catalysts have high activity and selectivity toward ring opening of C5 and C6 monocyclic molecules, but several reports show that C6 ring opening of molecule is enhanced by the use of bifunctional catalyst.[55,58–65] This also followed the mechanism of the C6 to C5 contradiction on the acid site and the openings of the C5 ring on the metal site.[55]

Ring opening of naphthenic molecule had been reported to occur via three distinct processes:

1. Non-selective mechanism involving the cleavage of the C-C bond of the ring with an equal chance of breaking any of the C-C bonds in the ring.

2. Selective mechanism involving the breaking of only unsubstituted C-C bonds usually known as dicarbene mechanism.

3. Partially selective mechanism involving the competing of both the non-selective and the selective mechanism as explained above.

The reaction condition employed were typically ~380°C and ~3 MPa pressure. However, temperatures between 250°C–400°C and pressures between 2–5 MPa were also claimed. Arribas et al. studied the conversion of tetralin under temperature conditions of 250°C–325°C in the presence of hydrogen gas as a co-feed.[66] It was observed that high activity of catalyst was obtained at high temperature reaching (>95%) and production of high cetane number products was also achieved reaching to about ~20% due to significant cracking activity expected to occur at high temperatures. However, this also relates to the topology of the zeolite support used as further argued in similar work.

Several literature results revealed that good support and active metal combination are very critical in achieving optimal ring opening reactions. The effect of Al_2O_3 and SiO_2-Al_2O_3 support was reported by on the activity of Rh-Pd catalyst for the conversion of decalin at 350°C and 3 MPa.[67] The gasoline conversion of the decalin and the selectivity of the ring opening products were increased using the SiO_2-Al_2O_3 support (Rh-Pd/SiO_2-Al_2O_3) to ~45.9% and ~55.8% respectively compared with ~19.3% conversion and ~5.4% selectivity over the Rh-Pd/Al_2O_3 catalyst. This signifies that promoting the acidity of a catalyst produces better activity. In another related investigation, it was revealed that Al_2O_3 support could make a better Rh-Pd catalyst for the conversion of methylcyclohexane at 400°C and 3.9 MPa compared with Rh-Pd/SiO_2 catalyst.[68] About ~99% conversion was obtained with Rh-Pd/Al_2O_3 compared with ~80% obtained with Rh-Pd/SiO_2 catalyst. Zirconia was also reported to be a good support for bifunctional catalyst.[69] Zirconia has the ability of fine tuning acidity by controlled W deposition. Nonetheless, zirconia is not a typical industrial catalyst support due to textural and mechanical constraints. However, Lecarpentier et al. and Lecarpentier revealed that Ir deposit on WOx/ZrO_2 support gives high performance bifunctional Ir/WO_3/ZrO_2 catalyst for selective ring opening reaction of methylcyclohexane.[58,70]

Dopants were also reported to enhance the selectivity and activity of a ring opening catalyst. The use of alkali metals to influence decalin conversion and selectivity to ring opening products was reported.[71] From the investigations, Ir/ H-β zeolite was exemplified as the catalyst material. When the catalyst was doped with various alkali metals, best conversion and selectivity were obtained with Ir/Rb/H-β doped catalyst about 100% conversion and 52% selectivity. Whereas, the least conversion and selectivity were obtained with Ir/Li/H-β doped catalyst, about 78% conversion and 37% selectivity. This showed that Rb species were more active compared to the other alkali species in the group. The dopants generally modify the acid sites of the H-β material and also reduce the cracking process of the reaction as shown in the paper. In another related paper, influence of Na addition on Pt-Ir/Al_2O_3 catalyst was studied on the reaction selectivity of ring opening of decalin and cyclopentane. It was revealed that the interaction between the Pt and Ir metals increases with the presence of the doped-Na and as a result, the catalytic properties of the catalyst was also modified. Increase ratio of (parameters of demanding/not demanding) reaction was achieved with the Na concentration. Three different doped catalysts were prepared (1%Pt-2%Ir-0.5%Na, 1%Pt-2%Ir-1%Na and 1%Pt-2%Ir-1.5%Na). When the catalysts was doped with various concentration of the Na, increase in conversions was obtained (~80%–95%) compared with ~40% obtained with the catalyst without the Na (Figure 2). Selective reaction mechanism was also favoured and formations of 2-methylpentane and 3-methylpentane were achieved from the methylcyclopentane reaction. About ~58% and ~26% selectivity were

respectively obtained compared with ~26% and ~16% respectively from catalyst without the doping Na.[72]

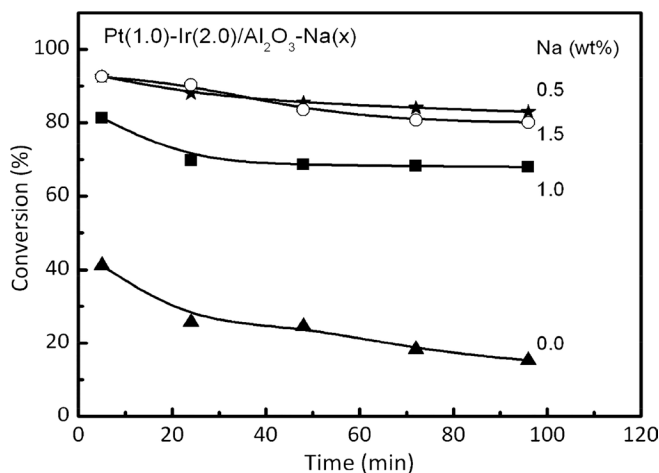Figure 2:   Conversion values as a function of time obtained in the methylcyclopentane reaction of Pt(1.0)-Ir(2.0)/Al$_2$O$_3$-Na(x) catalysts.[72]

2.2.2   Hydrogenation of aromatics to gasoline fuels

The shift in the valorisation of heavy hydrocarbons by ring opening processes could be very valuable in the production of high octane gasoline fuels. This could also be achieved through the ring cleaving of multi nuclear aromatic composition and their derivatives. The presence of polycyclic naphthenes and aromatic hydrocarbons in gasoline fuels are considered highly undesirable due to legislative restriction placed on them, particularly on benzene concentration in gasoline fuel because of serious environmental threat. The aromatic components are very much in FCC diesel fuel (~60% v/v) and do not only produce undesired emission exhaust gases but also affect the cetane number (Scheme 4).[73] Therefore, improving the quality of the fuel through selective opening of the aromatic ring with the formation of the same carbon atom as the starting hydrocarbon could be achieved. The ring opening is also profoundly relevant to the conversion of heavy hydrocarbon materials containing aromatics that allows the synthesis of high octane iso-praffins. Supported noble metal catalysts are widely known for the hydrogenation activity in aromatic hydrogenation at moderate reaction temperature and pressure.

The hydrogenation of benzene into cyclohexane had been reported in different published works.[74–77] There is scant or almost no literature on the hydrogenation ring opening of benzene as this is virtually not studied. However, data on the opening of cyclohexane could be accessed for easier evaluation but almost no work has

been performed on the direct conversion of benzene into paraffins. Onyestyák et al. reported the hydrogenation of benzene over Ru/Al$_2$O$_3$ catalyst at mild condition temperatures of 130°C–220°C.[74] The paper further shows that the hydrogenation consumption is elevated in the process relative to the ring opening of cyclohexane. The hydrogenation of the benzene occurs quite quickly and subsequently to the conversion of the generate cyclohexane and to the corresponding paraffin compound as illustrated in Figure 3.

In a related research conducted to study the conversion of benzene into ring opening using Ru/Al$_2$O$_3$, Ir/Al$_2$O$_3$ and Rh/Al$_2$O$_3$ catalyst, the reactions were shown to proceed in accordance with Figure 3, illustrating conversions passing through cyclohexane before ring opening. It was also revealed that there is a typical temperature dependence of the products yield over the main benzene conversion from the used catalyst.
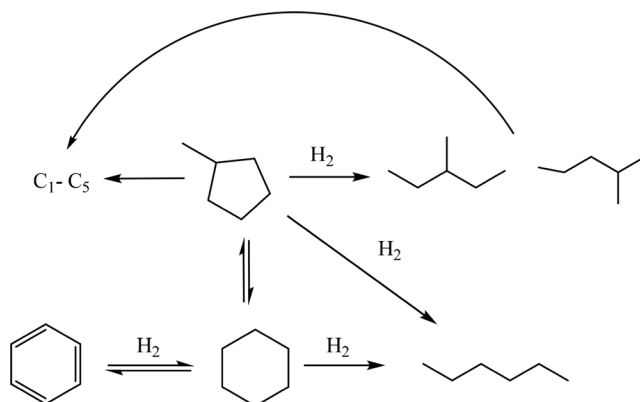

Figure 3: Benzene hydrogenation to cyclohexane and to the corresponding paraffin.

Other aromatic compounds also follow a similar mechanism with benzene, but additional possible reactions are observed and the schemes are more complicated than the ordinary benzene molecule. For example, the hydrodemethylation of toluene into cyclohexane occurs at low temperature (~100°C) over Pt catalyst and hydrodemethylation of toluene to benzene occurs at higher temperature (>380°C).[78] Fu et al. report the activity of Ni/HY zeolite catalyst in the conversion of toluene into ring opening products at 350°C–450°C and 3 MPa pressure.[79] The paper further reveals that the activity of the catalyst in this respect increases with an increase in nickel loading. The conversion of the tested toluene reactant increases with the increase in Ni content and so are the products of the aromatic ring opening (AO), while the product disproportionation (D) decreases greatly. HY and USY zeolites were also tested for comparison as presented in Table 1.

Table 1: Efficacy of Ni content on toluene hydrogenation activity.[78]

Catalyst	wt% Ni	%Conv.	%Selectivity	
			AO	D
NiHY-1	1.25	48.5	0.8	63.6
NiHY-2	1.5	59.1	4.6	47.7
NiHy-3	2.0	66.0	19.3	17.5
HY	–	0.63	–	–
USY	–	46.3	–	74.8

In another related study, a different type of catalyst was tested (Ni_2Mo_3N/zeolite) for the hydrogenation opening of aromatic compounds to observe changes using different zeolite supports.[80] The various zeolites (USY, H-beta, HZSM-5 and HMCM-41(Al)) were used for this evaluation and emphasis in the differential ring opening was made due to acidity and pore size of the catalyst. The pure Ni_2Mo_3N was reported to show low activity of hydrogenation with no ability to ring opening. Relatively high activity was obtained using H-Beta and USY zeolite supports in the opening of the aromatic substrate with about ~90% conversion achieved at 430°C and 3 MPa.

The ring opening of benzene molecule is presumed identical to that of cyclohexane.[81] However, strong adsorption of aromatic compound on the surface of catalyst may subsequently attribute to the blocking of acid site. Therefore, as the hydrogenation of cyclohexane molecules proceed usually quickly and selectively in many ring opening reactions, this might not be the same with the aromatic counterpart especially at high pressure. The benzene hydrogenation to cyclohexane molecule is usually the first in the ring opening of benzene. However, cyclohexane has a very low octane/cetane number and therefore need to further isomerise the molecule or open the ring to produce paraffin range hydrocarbon molecule. Several studies have been performed on hydrogenation, isomerisation and ring opening of aromatics.[75,77,80–84] Reaction performed by Shimizu et al. on benzene hydrogenation and isomerisation using Pt-supported solid acid catalyst at 250°C showed that benzene almost completely converted with all the Pt-supported catalyst.[75] However, reaction without any catalyst and with only sulphated zirconia showed very little hydrogenation. On the other hand, reaction with Pt/ZrO_2 showed no isomerisation to methylcyclopentane. About 46% isomerisation conversion was achieved using $Pt/SO_4^{2-}/ZrO_2$ catalyst which is much higher than what was observed with the other tested catalysts (Pt/SiO_2-Al_2O_3, Pt/HY-5.6 and Pt/HM-10). The reaction isomerisation of the methylcyclopentane did not occur using either ZrO_2 and or Pt/ZrO_2 while HY-5.6 and HM-10 showed only 2% and 30% conversions,

respectively. SO_4^{2-}/ZrO_2 catalyst showed increase isomerisation percentage of 46.2%. This shows that benzene hydrogenation and isomerisation at 250°C are better on the Pt/HY-zeolites and Pt/H-moderate catalyst with the isomerisation activity only significant with SO_4^{2-}/ZrO_2 which make the sulphated group required for the cyclohexane isomerisation. In a related study, Au-Pd/SiO$_2$-Al$_2$O$_3$ catalyst was used to study the hydrogenation of toluene and naphthalene.[82] It was shown that hydrogenation of toluene is more difficult compared with naphthalene because of the decrease in resonance energy per aromatic ring and also differences in π-electrons cloud density due to the attached methyl group. Five different supports were used for the hydrogenation of toluene which involves varying the Al content (%) (SA-0, SA-8, SA-14, SA-28 and SA-100). The SiO$_2$-Al$_2$O$_3$ catalyst carrier showed a clear enhancement in the hydrogenation of the toluene compared with the Al$_2$O$_3$ and SiO$_2$ counterpart system under the selected conditions 5.0 MPa pressure, 523 K temperature and 41.2 h^{-1} WHSV. The hydrogenation with SA-8, SA-14 and SA-28 significant turnover frequencies (TOF) compared with other tested catalyst is presented in Figure 4 which is abstracted from Venezia et al.[82] Au in hydrogenation activity has also been previously claimed because Au d-bands nearly have no ability of dissociate hydrogen molecules.[85–91]
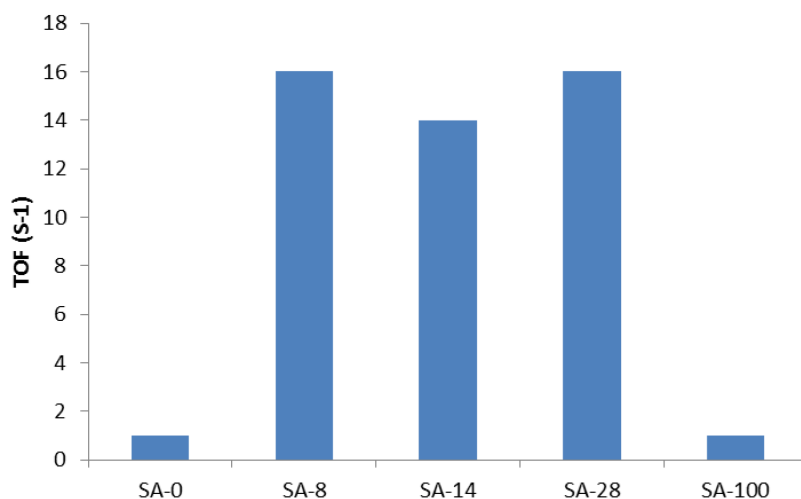

Figure 4: Calculated TOF for the toluene hydrogenation.[82]

Lin et al. performed the hydrogenation of benzene over Pt dispersed on SiO$_2$, η-Al$_2$O$_3$, SiO$_2$-Al$_2$O$_3$, TiO$_2$ and powdered Pt catalyst.[77] It was shown that the activation energies and the reaction order of the various reactions were independent of the used support. Values between 10–13 Kcal mol^{-1} were obtained with partial pressure dependencies $\sim 0.6 \pm 0.1$ on H$_2$ and 0.1 ± 0.1 on benzene 317 K and 356 K temperatures respectively. The acidic support catalyst produced high

activities at 333 K under 50 torr benzene and 685 torr H_2. A frequency turnover of ~0.078 s^{-1} was achieved with Pt/TiO_2 catalyst compared with 0.015 s^{-1} achieved with Pt/η-Al_2O_3 catalyst. The support acidity decreases in the order 0.95% Pt/TiO_2 > 0.24% Pt/SiO_2-Al_2O_3 > 0.96% Pt/SiO_2 > Pt/η-Al_2O_3. However, a large increase was observed under 35 torr benzene pressure.

Catalyst treatment was also reported to enhance the hydrogenation activity of aromatic hydrogenation. Studied conducted by Ali et al. on benzene and toluene hydrogenation into cyclohexane and methylcyclohexane respectively between 50°C–250°C temperature range was exemplified.[83] The investigated catalyst 0.35% Pt/Al_2O_3 was modified by using second metals Ir, Rh, Re and U and then treated via chlorination and fluorination with different halogenation contents of 1 wt%, 3 wt% and 6 wt%. The study showed that all the tested catalysts possessed good catalytic activities at ~125°C–150°C temperature range except for Rh which is very active even at room temperature. Treatment of the catalyst with Ir or Re enhanced the hydrogenation activity of the Pt catalyst, while only Ir/Al_2O_3 and Re/Al_2O_3 showed lower hydrogenation activity compared with Pt-Ir/Al_2O_3 and Pt-Re/Al_2O_3 respectively. The activity follows the order Ir/Al_2O_3 & Re/Al_2O_3 < Pt, Re & Ir < Pt-Ir/Al_2O_3 & Pt-Re/Al_2O_3. The use of U inhibit the activity with Pt-U/Al_2O_3 showing even lower activity than Pt/Al_2O_3 but higher than U/Al_2O_3. All the halogenated catalysts promote the activity of the catalyst. Catalyst with 3 wt% F or Cl showed highest activities for both benzene and toluene hydrogenation. This may be due to improving H_2 spillover and increasing metal dispersion into the support. The 6 wt% treatment may have decrease the H_2 spillover by decreasing the number of –OH group as H_2 moves to active metal crystalline. The addition of Cl and F enhanced the catalyst activity to 21% and 18% benzene, and 25% and 30% toluene respectively from 4.2% and 5.4% benzene and toluene at ~150°C temperature. Halogen treatment on the Pt-Rh/Al_2O_3 showed an exceptionally higher activity for both benzene and toluene. Benzene and toluene hydrogenation reached >90% and 100% respectively even at lower temperature (50°C) which was maintained up to ~175°C. Recently, Soni and Sharma have employed nano-sized Pd-Clay (montmorillonite) for the hydrogenation of squalene surface modification of the clay and metal intercalation simultaneously occurred during wet impregnation.[92] The Pd-nanoparticles-intercalated clay with a dominating Pd(1 1 1) facet showed the highest reactivity and selectivity. The catalyst was stable with very low Pd leaching ($\approx$ 0.03 ppm) and was recyclable without losing any significant catalytic activity. In general, the hydrogenation activities of the tested catalyst highly improved in the presence of the halogenation treatment compared to un-halogenated ones. Some recently published literature identified Ni/Co-natural clay systems as good candidates for the upgrading reactions like hydrodeoxygenation (HDO) and/or hydrodenitrogenation (HDN) encountered during fuel production.

According to Soni et al., the HDO process provided higher carbon atom economy and energy value over decarboxylation/decarbonylation, while further reducing the formation of greenhouse gases such as CO_2 and CH_4.[93] Total yield of saturated hydrocarbons from algae oil valorisation was 84–86 wt% with similar selectivity. The HDO rates of different fatty acids present in the algae oil were independent of the fatty acid chain length. The catalysts were cost-effective and recyclable, and metal leaching during hydroprocessing was less than 1 ppm in all cases. This process is advantageous in terms of metal-to-substrate ratio, use of solvents and their concentration, and comparable HDO selectivity over the previously reported catalysts. A hydroprocessing reaction was also performed under solvent free conditions, which could be useful in industrial applications. Therefore, the clay-supported catalysts have good refining potentials for upgrading fuel feeds.

3.   CONCLUSION AND OUTLOOK

Hydrogenation is an important catalytic process recently prioritised by the petroleum refineries for the production of high-quality gasoline suitable for application in modern and re-configured automobile engines. Mechanistically, the process proceeds through C-C bond cleavages involving hydrogen addition, saturation of C=C bonds in olefins/aromatics, ring opening of cyclic compounds and isomerisation in certain circumstances.

Catalytic parameters identified very influential during the process include hydrogen pressure, reaction temperature, catalyst nature and composition, and the nature of the reaction feed. Metal promoted oxides and modified zeolites have so far demonstrated good hydrogenation activity. However, the challenges of catalyst deactivation by coke precursors and consequent pore-blockage are not yet resolved.

There are numerous issues that should be fully evaluated in order to actualise the overall process in economic and scientific efficiency. The role of catalyst preparation conditions such as hydrothermal conditions, impregnation/deposition/precipitation and the subsequent calcination conditions on the generation of catalytically active sites and their associated stability under variable reaction conditions must be fully explored. Hydrogenolysis is a common problem encountered with the oxides supported Pd, Pt and Ni catalysts especially at higher loadings exceeding 5 wt%. It is therefore very vital to establish the optimal and workable metal loadings. Clearly, hydrogenolysis of the hydrocarbons generates free radical species that can trigger chain reactions and consequent evolution of unwanted gaseous products with carbon numbers below the gasoline range.

Zeolite catalysts should be designed in the nano- and hierarchical (i.e., mesoporous scale) forms in order to fully eliminate the problems of diffusional limitations. When the diffusion of reactants/reaction products is hindered, cracking and carbonaceous deposition becomes prominent and the catalytic activity decays rapidly. Another area to be explored includes the influence of Si/Al ratio (i.e., zeolite acidity) and topological properties on the overall reaction mechanism and the yield of desired gasoline range hydrocarbons.

4.   ACKNOWLEDGEMENTS

5.   REFERENCES

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